Laboratory Name: National Renewable Energy Lab
B&R Code: KC020103

FWP and possible subtask under FWP:
Novel Ordered Semiconductor Alloys

FWP Number:
ERWER20

Program Scope:
The research on this project involving ordered semiconductor alloys combines experimental and theoretical efforts aimed at understanding long-range order in isovalent semiconductor alloys. The project includes: (i) MOCVD growth of III-V alloys such as GaP/InP, growth of hybrid organic-inorganic superlattices (ii) Raman, modulation reflectance, photoluminescence, NSOM, Magneto-PL and reflectance-difference spectroscopy studies of ordering in the above systems, and (iii) first-principles theoretical studies of surface-induced, epitaxially-induced and bulk ordering in various alloys as well as on the electronic bandstructure changes and lattice dynamics changes induced by ordering. The project includes structural studies based on transmission electron diffraction and X-ray scattering for determining the order parameter, thermal expansion coefficient, and involves use of DOE synchrotron facilities.

Major Program Achievements (over duration of support):
Developed the concept of partial ordering, statistical distribution function and order parameter, orientational superlattices, effective mass anisotropy, pyroelectric behavior and spontaneous electric fields. Developed theoretical models for surface induced ordering. First structural and electronic measurements of order parameter. Developed ability to tailor order parameter and consequent electronic properties. Developed the understanding of the lattice dynamics and phonon spectrum of ternary alloy GaInP through control of order parameter. Developed the understanding of the influence of microstructure on the optoelectronic properties of the spontaneously ordered alloy. This work led to the first experimental demonstration of amphoteric (negative and positive) refraction at an orientational domain boundary, and first demonstration of giant tuning of bandgaps possible in hybrid semiconductors..

Program impact:
Almost all the present understanding of the electronic properties of spontaneously ordered semiconductor alloys has been pioneered by this program. This understanding is now being exploited for engineering advanced solar cells, HBT transistors for cellular communications, and for novel polarization sensitive optical devices, as well as for providing insights into the exciting phenomenon of negative refraction

Interactions:
University of Houston (S.C. Moss), X-ray and synchrotron studies of order parameter.
Rutgers University (J. Li), Novel Hybrid organic-inorganic superlattices
NHFML-Florida State University, High Field Magneto-PL Studies of Ordered Alloys
Univ. of Erlangen (G. Doehler), Polarization sensitive devices based on ordered alloys.
North Texas University, Ordering in Antimonide Alloys

Recognitions, Honors and Awards (at least partly attributable to support under this FWP):
Our paper on "Amphoteric Refractions" was cited as one of the Top 15 Physics Stories of 2003 as well as cited in Physics Today, 2003. Over 110 Physical Review publications and over 14 Physical Review Letters on the subject of Spontaneous Ordering, over 26 Invited Talks.

Personnel Commitments for FY2005 to Nearest +/- 10%:
B. Fluegel (35%), Y. Zhang (50%), W. McMahon (50%), Mascarenhas 30% .

Authorized Budget (BA): FY04 $634, 000 FY05 $609, 000 FY06 $597, 000

Laboratory Name: National Renewable Energy Lab
B&R Code: KC020202

FWP and possible subtask under FWP:
Physics of isoelectronic co-doping

FWP Number:
ERWER2B

Program Scope:
Isoelectronic co-doping GaAs and GaP with Bismuth and Nitrogen is proposed as a novel method for regularizing the abnormal alloy behavior that is observed in these materials when they are doped with Nitrogen alone. The technique will lead to enhancements in 1) the solubility of isoelectronic dopants, and 2) carrier mobilities as compared to doping with Nitrogen alone. The use of the technique will make it possible in several situations to overcome the limitations imposed by semiconductor alloy constraints on the design of some technological important devices such as such as solar cells, lasers and LED's. Most importantly, it will enable the growth of photonic devices on Silicon substrates. The proposed research will advance the basic understanding of the Mott-transition in heavily doped semiconductors as well as help unravel the fundamental mechanisms of alloy formation.

Major Program Achievements (over duration of support):
First observation of Nitrogen resonant level l, of effective mass anomalies, of giant bandgap bowing in GaP, and of the impurity band model. Invention of the concept of isoelectronic co-doping for regularizing optoelectronic properties of GaAs:N and GaP:N. First successful incorporation of Bi into GaAs that showed isoelectronic trap like behavior. The technique of resonant light scattering for probing localized electronic states was pioneered under this project. The research has also led to the first identification of 1) spatially resolved impurity pairs in alloys 2) of giant spin-orbit bowing in semiconductors.

Program impact:
The research resulting from this project has set the trend for most of the current perspective of the mechanisms underlying the giant bandgap bowing in dilute Nitride Alloys. A patent with 165 claims for optoelectronic devices based on the invention of the concept of isoelectrnic co-doping has been awarded and the research has resulted in 47 publications.

Interactions:
Univ. of North Texas, Growth of GaP:N and GaAs:N
Univ. of British Columbia, Growth of GaAs:Bi
Univ. of Montreal, Rutherford Backscattering studies.
Sogang University (Seoul, Korea), LPE growth of GaAs:Bi:N, GaP:Bi:N
Sandia National Labs, Growth of GaAsN Quantum Wells.
National High Magnetic Field Lab., Florida State Univ., High Magnetic Field Studies
Institute of Semiconductors (Beijing), High Pressure studies.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Seven Invited Talks, 5 Invited Papers, 40 research publications (2 Phys. Rev Lett.), I patent, 2 book chapt.

Personnel Commitments for FY2002 to Nearest +/- 10%:
Y. Zhang(10%), 1.5 Postdoc, A. Mascarenhas (30%), B. Fluegel (30%)

Authorized Budget (BA) for FY04, FY05, FY06:
FY04 $350,000 FY05 $320,000 FY06 $363,000

Laboratory Name: National Renewable Energy Laboratory
B&R Code: KC020301

FWP and possible subtask under FWP:
Carbon Nanotube Membranes and Adsorbents

FWP Number: ERWER0L

Program Scope:
Investigate basic science of nanotube membranes and materials in gas separation and fuel cell applications. Explore electrocatalysis on nanotube-supported catalysts. Understand the adsorption, transport, and reactivity (gas phase and electrochemical) of molecules such as H_2, H_2O, CH_4, and CO_2 on the surfaces of carbon nanotube materials and membranes, and on carbon nanotube materials decorated with catalysts. Develop synthetic methods to produce desired doped and metal-decorated materials, electrodes and crystals.

Major Program Achievements (over duration of support):
First synthesis of boron-doped nanotubes by laser vaporization after discovery of novel catalyst. Determined p-type conductivity by ^{13}C nmr spectroscopy. Chemical vapor deposition growth of carbon single-wall nanotubes (SWNTs) near equilibrium was followed using Raman spectroscopy, permitting the first experimental determination of the Gibbs free energy of SWNT formation. A new synthetic method was developed which combines the best aspects of conventional laser and arc growth methods and offers high production rate of low-defect density nanotubes. Platinum-doped nanotubes synthesized by this method show improved activity as fuel cell electrodes. SWNT/polymer composite membranes offer dual transport pathways for improved performance over either material alone. Temperature programmed desorption studies show higher binding energies for CO_2 than for CH_4. Purified, laser-grown carbon single-wall nanotube (SWNT) powders strongly bind CO_2 and only weakly adsorb CH_4 at room temperature and 500 torr. Volumetric measurements show the same result at 200 K, and are in contrast to the literature data for graphite that shows only weak CO_2 adsorption.

Program impact:
Advanced the understanding of transport and reactivity of important energy-important small molecules on nanotube surface, membranes, and electrodes. Developed methods to fabricate carbon nanotube membranes. Explored metal-decorated nanotube materials for use in catalysis and fuel cells. Measured the thermodynamics of single-wall carbon nanotube growth. Advanced nanotube growth science and technology.

Interactions:
Internal - OS/DMS Theory (S. Zhang); DOE/EERE/HFCIT program on H_2 storage; OS/DCS Nanoscience "Intermediating Quantum Dot communication with carbon nanotubes and proteins". External - ORNL, LLNL, NIST, NASA, Rochester Institute of Technology, Rice U., U. of Quebec, U. of Michigan, Caltech, Stanford U., U. Pennsylvania, Penn State, North Carolina State University, Air Products and Chemical, Inc.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
Heben - International Energy Agency expert on hydrogen storage; President's Hydrogen Technical Advisory Panel Year 2000 Research Success Story award; Lead of DOE/EERE Center of Excellence on Carbon-based Hydrogen Storage; Organizer of symposia on Hydrogen Materials at: Fall 2004 MRS meeting, Summer 2005 International Partnership for Hydrogen Energy meeting: Spring 2006 MRS meeting: Summer 2006 ECS Meeting.
Dillon – Organizer Fall 2005 MRS meeting. NSF, MRSEC Review Panels. Plenary speaker honoring Claire Boothe Luce, who established foundations to promote women in science, 2003. Nominated/accepted for the National Academy of Engineering Symposium on *Frontiers of Engineering*, 2006. Keynote lecture at the 2005 Taiwan Symposium on Hydrogen Storage in Carbon Nanomaterials, Oct. 18, 2005 Taipei, Taiwan. Dillon/Heben - ~ 28 invited talks since 2001.

Personnel Commitments for FY2005 to Nearest +/- 10%:
M.J. Heben – PI (10%); A.C. Dillon (10%); C. Engtrakul (50%); S.H. Lee (30%) .

Authorized Budget (BA) for FY04, FY05, FY06: FY04 BA $234,000 FY05 BA $215,000 FY06 BA $215,000

Laboratory Name: National Renewable Energy Laboratory
B&R Code: KC02.0103

FWP and possible subtask under FWP:
Overcoming the doping bottlenecks in semiconductors

FWP Number:
ERWER0K

Program Scope:
The objective of the project is to understand doping limits in various semiconductors and to propose ways to overcome these limits, which is essential to the design of a wide range of new semiconductor devices such as high-efficiency solar cells, blue and UV LEDs and lasers, and detectors with impacts on both nanotechnology and next-generation integrated circuits.

Major Program Achievements (over duration of support):
Developed a theory for equilibrium doping from which one can predict the doping properties of a wide range of semiconductors and alloys. Pioneered the theories for non-equilibrium doping. A number of recent important experimental observations are explained, which include (i) ultrahigh doping of silicon, (ii) p-type conductivity of zinc oxide, (iii) high nitrogen solubility and clustering in gallium arsenide, (iv) p-type and bipolarly dopable transparent conducting oxides, (v) n-type diamond, (vi) irradiation defects, and (vii) defects and doping of quantum dots. Our studies are instrumental to the development of basic understanding of the doping bottlenecks, as well as providing practical recipes to overcome such bottlenecks in wide-gap semiconductors. Band structure engineering by impurities represents another important achievement. The studies of oxygen induced direct-gap, visible light-emitting silicon, band gap tuning by hydrogen in gallium arsenide nitride, and icosahedral symmetry through twinning in silicon nanostructures have added new dimensions to the project.

Program impact:
Eighteen papers were published in Physical Review Letters since FY00. Nature's "Materials Update" had a feature article on Aug. 8, 02 about our proposal of direct-gap, light-emitting silicon. Physical Review Focus reported our work of icosahedral silicon quantum dots on July 2, 04. Overall, our studies provide insights on the microscopic origin of the doping limits in semiconductors, extend the physics of semiconductor point defects into the non-equilibrium growth regime, and suggest new ways to overcome the doping limits, as well as new ways to modify the properties of the host materials. We have been recognized as a leader in the theoretical study of defects in semiconductors: e.g., this year Shengbai Zhang has been elected the chair for the Gordon Research Conference: Defects in Semiconductors in 2010.

Interactions:
C. G. Van de Walle, Polo Alto Research Center, Inc.; D. C. Look, Wright State University

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):
About 30 invited talks in international conferences since 1999
DOE/BES Chunky Bullet Award, 2002

Personnel Commitments for FY2007 to Nearest +/- 10%:
Shengbai Zhang (Principal Investigator) 5%
Su-Huai Wei (co-PI) 5%
Jingo Li (post-doc) 50%
Chang-Youn Moon (post-doc) 100%
Lixin Zhang (post-doc) 100%
Damien West (post-doc) 100%

Authorized Budget (BA) for FY04, FY05, FY06:
FY04: $390,000 FY05: $374,000 FY06: $382,000

Laboratory Name: National Renewable Energy Laboratory
B&R Code: KC0202030

FWP and possible subtask under FWP:
Understanding Molecular Hydro Absorbents: A First Principles Theory for van der Waals Interactions

FWP Number:
ER21

Program Scope:
The scope of the program is to develop an effective and efficient first-principles approach and to apply the approach to study van der Waals interactions between molecular hydrogen and realistic molecular-hydrogen absorbents, in order to provide the fundamental knowledge for meeting the grand challenge of developing a secure, compact, lightweight, and economic method of storing hydrogen fuel onboard vehicles.

Major Program Achievements (over duration of support):
This is a new project started at the end of August 2006. While it is still too early to report any major program achievement, the project is doing well according to the plan. We have recruited all the personnel required.

Program impact:

Interactions:
Andrew Williamson, Livermore National Laboratory

Recognitions, Honors and Awards (at least partly attributable to support under this FWP or subtask):

Personnel Commitments for FY2007 to Nearest +/- 10%:
Shengbai Zhang (Principal Investigator) 5%
Yong-Hyun Kim (co-PI) 40%
Yiyang Sun (post-doc) 100%
Kyuho Lee (post-doc) 100%

Authorized Budget (BA) for FY04, FY05, FY06:

FY06: $300,000

Laboratory Name: National Renewable Energy Lab
B&R Code: KC0202030

FWP and possible subtask under FWP:
Million-Atom Nanostructure Architecture

FWP Number: ER5A.1000

Program Scope: Whereas contemporary electronic structure theory is largely dealing with molecules and clusters containing up to ~100 atoms in the computational cell, such recent experimental advances now pose staggeringly more difficult challenges to theory and simulation efforts. The challenges emerging from such experimental studies are in three areas: (i) the need to address *large* single nanostructures, in the range of 10^3 -10^6 atoms, (ii) the need to deal with the *complexity of the underlying electronic phenomena*, including quantum entanglement, excitonic complexes, exchange-induced fine-structure, Coulomb and spin blockades, and unusual decay mechanisms of excited states (e.g., multi exciton generation from one photon), and, (iii) the emergence of *nanostructure systems*, involving combined *3D architectures* of quantum dots, wires and wells (0D, 1D, 2D, respectively), as the main vehicle for nano devices and nano technology. Indeed, experiments seem to currently be far more advanced than theory in these areas of nanoscience. This project involves a team of physicists, computer scientists and mathematicians from three national laboratories and a University developing the blueprint for the next generation methodology of theory of million-atom nanostructure architectures. This project involves five research directions: (a) Develop an atomistic pseudopotential approach capable of addressing the single-particle problem of million-atom nanostructures; (b) Develop a many-body (configuration interaction / Bethe-Salpeter based) approach for the same nanostructures; (c) Study the complex nanoscience phenomenology of inter-band and intra-band optical spectra, quantum entanglement of the many-particle wave functions, multi-exciton complexes, Coulomb- and spin-blockade, and excited-state carrier relaxation , and explain the recent experimental observations in these areas, (d) address complex nanostructure *systems* combining 0D, 1D and 2D building blocks, and (e) offer design capabilities, via the "inverse band structure" approach, to predict the structure of systems that have prescribed electronic properties.

Major Program Achievements (over duration of support): Development of new computational and theoretical approaches to items (a) and (b) above, (ii) the application of these new methodologies to most of the physical phenomena described under item (c) for self-assembled million-atom InAs/GaAs prototype nanostructures, (iii) the calculation of inter-band and intra-band absorption spectra, Coulomb blockade effects, fine-structure splittings, and carrier multiplication rates [item (c) above] in PbSe colloidal quantum dots containing a few thousand atoms, (iv) the study of radiative recombination lifetime, emission polarization, and multi-exciton emission spectra in CdSe colloidal quantum dots [item (c)], and (v) the prediction of electron localization and wave-function entanglement in complex, three-dimensional CdSe/CdTe nano dumbbells [item (d)].

Program impact: Theoretical explanation of the main physical effects observed spectroscopically in self-assembled quantum dots, including excitonic spectra and its dependence on size and shape; multi-exciton energies; exchange-splitting; excitonic fine-structure; intra-band transitions; effects of electric fields on dot; quantum entanglement in dot molecules; singlet-triplet splitting .For colloidal dots we explained Auger relaxation dynamics and mechanism of multi-exciton generation.

Interactions: This is a collaboration between NREL and LBNL, ORNL and U. of Tennessee

Recognitions, Honors and Awards (at least partly attributable to support under this FWP: In the 2.5 years since program started published 44 papers, including 6 in Phys Rev Letters, and delivered 12 Invited Talks, including 2 March Meeting Invited talks.

Personnel Commitments for FY2005: A. Zunger (Lead-PI; 15 %); A.Franceschetti (50 %); G.Bester (100%); two post docs (100%)

Authorized Budget (BA): FY04: $485,000 FY05: $585,000 FY06: $575,000

Laboratory Name: National Renewable Energy Lab
B&R Code: KC0202030

FWP and possible subtask under FWP:
Semiconductor Theory

FWP Number:ER62.0101

Program Scope:

Semiconductor-based High-Technology involves a rather complex mix of materials, phases and interfaces that are very hard to study and optimize experimentally .For example, photovoltaic solar cells, light-emitting diodes, solid-state lasers and lightning as well as semiconductor-based sensors often requires a few layers of different materials, surfaces and interfaces, random , (partially) ordered alloys, as well as n- and p-type doping. Understanding of the operation of the system and optimizing it requires disentangling the physical behavior of the components, an endeavor that has historically proven to be experimentally very difficult, if not impossible. The role of our project " Semiconductor Theory " is to develop a fundamental understanding of the semiconductor materials and underlying physical phenomena that control such semiconductor-based energy technologies, allowing better design and control. The physical phenomena we address are: (a) *Bulk physics*--the basic electronic structure, optical and mechanical properties of the crystalline building blocks of semiconductor material science. (b) *Surfaces and interfaces of semiconductors*--surface-induced ordering, interfacial interdiffusion and their effect on electronic properties. (c) *Defect physics of semiconductors*--the way that point-defects affect the electronic and transport properties (d)do*pability of semiconductors*--understanding what does it take to introduce electrons and holes into a material (e) *Physics of semiconductor alloys*--optical bowing, short range order, clustering and phase-diagrams.

Major Program Achievements (over duration of support) . We have developed novel theoretical techniques needed for the above plan ,including novel pseudo potentials approaches, as well as new schemes for Exchange and Correlation. We also developed Mixed-Basis Cluster Expansion (MBCE) methods to study alloy phase stability, as well as the Inverse Band Structure (IBS) method to survey a large number of materials, searching for the one with prescribed properties. Current work includes: (1) prediction of optical and dielectric properties of semiconductor quantum dots, wires, and films (CdSe, GaAs, InP); (2) first-principles prediction of alloy thermodynamic quantities (e.g., phase-diagrams, short range order) for semiconductors and metallic alloys; (3) calculation of electronic properties of novel nitride alloys; (4) prediction of properties of unusual ternary materials, e.g., ordered vacancy compounds; (5) physics of unusual superlattices (e.g., InAs/GaSb); and (6) properties resulting from combining semiconductivity with magnetism (e.g. (Ga, Mn) As).

Program impact: Established a systematic and quantitative theoretical approach to predict novel alloy phases and their thermodynamic properties from first-principles calculations; developed the Inverse Band Structure approach for finding materials with designated properties; established basic theory of semiconductor alloy ordering and bowing.

Recognitions, Honors and Awards (at least partly attributable to support under this FWP: John Bardeen Award of TMS (2001); A. Rahman award of APS(2001); published over 100 papers in Phys Rev and Letters; 23 Invited papers in leading conferences.

Personnel Commitments for FY2005 A.Zunger (lead PI; 10 %); 3 post docs (100%).

Authorized Budget (BA) FY04: $340,000 FY05: $350,000 FY06: $340,000